Interest of modelling heat transfer inside a reactor to estimate kinetic parameters

Nadiarid Jiménez [a], Philippe Bohuon [b], Manuel Dornier [b], Catherine Bonazzi [c], Fabrice Vaillant [d]

[a] *Universidad de Costa Rica, San José, Costa Rica (nadiarid.jimenez@ucr.ac.cr)*
[b] *Montpellier SupAgro, UMR Qualisud, Montpellier, France (philippe.bohuon@supagro.inra.fr, manuel.dornier@supagro.inra.fr)*
[c] *INRA, UMR1145 Ingénierie Procédés Aliments, Massy, France (catherine.bonazzi@agroparistech.fr)*
[d] *CIRAD, UMR Qualisud, Montpellier, France (fabrice.vaillant@cirad.fr)*

ABSTRACT

A space-and-time dependent model was developed for a reactor. The model, which combines heat transfer and chemical reaction, was intended to identify kinetic parameters under non-isothermal conditions for low-intermediate moisture foodstuff. In particular, the model was used to evaluate the effect of high temperature heat treatments (100–140 °C) on anthocyanins degradation in blackberry juice – quartz sand system at low water activity (a_w 0.34). The coupled transport equations were solved using Comsol® calculation code. Kinetic and thermal parameters were identified with a nonlinear regression method. The relevance of this approach was assessed by comparison between the kinetic parameters estimated as described before (heterogeneous assumption) and the parameters identified by considering a homogeneous temperature distribution inside the reactor. The results showed no significant difference between the anthocyanins degradation reaction rate constant ($k_{120°C}$) for the heterogeneous ($3.29\pm0.05\times10^{-3}$ s^{-1}) and the homogeneous ($3.5\pm0.3\times10^{-3}$ s^{-1}) assumption. And a slight difference was found between the activation energies (E_a) for the heterogeneous (95±5 kJ mol^{-1}) and the homogeneous (108±7 kJ mol^{-1}) identification. Therefore, the use of the developed model allowed a slight improvement in the identification of the kinetic parameters. However, the assumption of a heterogeneous distribution of temperature inside the reactor is valid for the identification of kinetic parameters with high orders of magnitude.

Keywords: Reaction kinetics; parameter estimation; heat transfer; non-isothermal; high temperature

INTRODUCTION

Kinetic parameter estimation of compounds in low-intermediate moisture food processed at high temperature (T > 100 °C) represents a challenge since two aspects must be considered: (*a*) A non-isothermal condition (time-dependent), where heating-up and cooling-down times play a role in the reaction, and the concentration of the compound of interest is a function of the varying temperature, which is in turn a function of time [1]; and (*b*) a unsteady-state conduction-heat condition (space-dependent), where the heat distribution within the product depends on the thermophysical properties of the food and the thermal parameters of the system. Both the thermal and kinetic parameters should be identified by nonlinear regression methods, as well as the confidence intervals of the parameters [2].

There is as yet not much work published on how quality changes are related to aspects such as heat and mass transfer, and this is clearly needed for a better product and process design [1]. Some examples are: for thiamine degradation in canned white tuna [3] and in canned pea puree [4]; for microbial inactivation in canned pea puree [5]; for thermal degradation of asparagus texture [6]; for enzyme inactivation in cylindrical vegetables using a finite element method [7]; for lipoxygenase inactivation during heating of cut green beans [8]. And more recently, for thermal degradation of anthocyanins in canned grape pomace [2], and in a mixture of grape anthocyanins with wheat flour at three different water contents [9].

In high temperature heat treatments, modelling of heat transfer allows a more reliable assessment of the temperature distribution in the product during treatment. Therefore, it enables the identification of limiting phenomena such as the heterogeneity of temperature in the product and the consideration of irreducible coupling phenomena between heat transfers (convection, conduction) and degradation kinetics.

In the context of non-isothermal processing at high temperature, the objectives of this study were, firstly, to propose an experimental procedure and numerical analysis to estimate kinetic parameters for thermal

degradation of functional compounds in low-intermediate moisture food, using anthocyanins in blackberry as a model of functional food; and secondly, to compare the proposed method with the simplified method where a homogeneous temperature distribution is considered.

MATERIALS & METHODS

Experimental method:

Blackberry juice – quartz sand samples at low water activity (a_w 0.34) measured at 25 °C were heated at 100, 120 and 140 °C in a hermetically stainless steel reactor (inner diameter 50 mm and the inner height 7 mm), designed and built by Jimenez *et al.* (2010). The reactor was designed for fast heating and cooling cycles without mass transfer of water and oil, which could interfere in component degradation [10]. Sample temperature within the closed reactor was recorded with a thermocouple located at the geometrical centre of one compartment and connected to a data logger. Total monomeric anthocyanin content ($A^{(t)}$) in samples was determined by the pH differential method [11].

Numerical method:

Homogeneous assumption. The anthocyanins content ($A^{(t)}$) decrease during heat treatment was described in terms of irreversible first-order kinetic:

$$dA^{(t)}/dt = -k_A\ A^{(t)} \tag{1}$$

The rate constant k_A (s^{-1}) varied with the system's absolute temperature, $T^{(t)}$ (K), according to the Arrhenius law, as follows:

$$k_A = k_{ref}\, exp\left[\frac{E_a}{R}\left(\frac{1}{T^{(t)}} - \frac{1}{T_{ref}}\right)\right] \tag{2}$$

where, k_{ref} (s^{-1}) was the rate constant at the reference temperature, E_a was the apparent activation energy (J mol^{-1}), and R the gas constant (8.314 J mol^{-1} K^{-1}). The reference temperature was chosen to be in the middle of the studied temperature range (T_{ref}=120 °C). The anthocyanins degradation during heat treatment was taken into account in equation (1). Hence, the average A value, predicted at time t ($A^{(t)}$), was calculated by time integration, as follows:

$$\hat{A}^{(t)} / A^{(0)} = \exp(-k_{ref}\ \beta_A) \tag{3}$$

where β_A is the time-temperature history for A:

$$\beta_A = \int_0^t \exp\left[\frac{-E_a}{R}\left(\frac{1}{T^{(t)}} - \frac{1}{T_{ref}}\right)\right] dt \tag{4}$$

The integral of equation (4) was calculated as the direct analytical integral of the cubic smoothing spline function (MATLAB®, The MathWorks Inc., Natick, MA, USA). There were two parameters (k_{ref} and E_a) to be estimated from the collected data.

Heterogeneous assumption. A space-and-time dependent model was developed for the reactor. The model, which combines heat transfer and chemical reaction, was developed to identify kinetic parameters under non-isothermal conditions. The 3D domain is defined with two sub-domains: the foodstuff and the stainless steel reactor (**Figure 1**). Heat conduction was assumed to take place inside the cell and sample, while Neumann boundary conditions were applied to the reactor outer surface in contact with hot oil (convective heat flux, h_{oil}) and the cell inner surface in contact with foodstuff (thermal contact resistance, $R_{contact}$). The coupled transport equations were solved using the COMSOL Multiphysics™ calculation code. The system parameters (h_{oil} and $R_{contact}$) and the kinetic parameters, degradation rate constant (k_{ref}) and activation energy (E_a), were estimated using the nonlinear least squares regression methods with the Levenberg-Marquardt algorithm by "lsqcurvefit" function (MATLAB®, The MathWorks Inc., Natick, MA, USA). To compute the 95% asymptotic confidence intervals of each parameter, "nlparci" function was used as recommended by Dolan et al. (2007) [12].

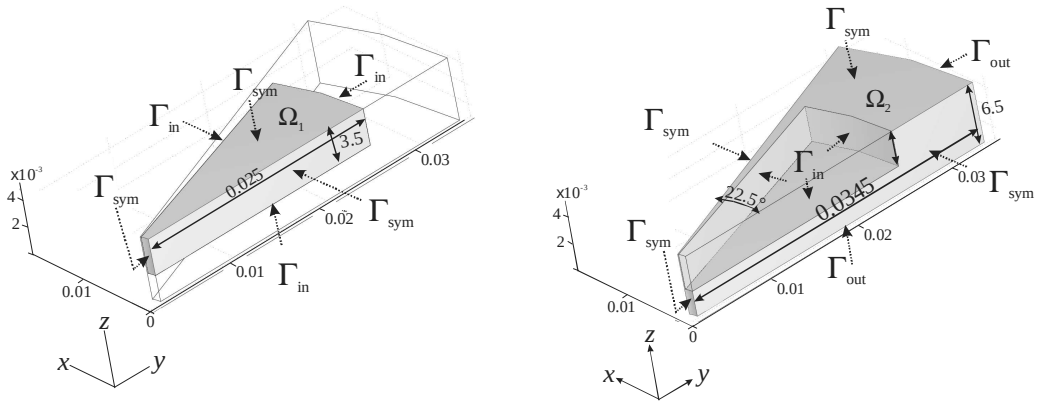

Figure 1. Schematic view (not to scale) of the computational domain 3D; Ω_1: blackberry juice – quartz sand sample; Ω_2: stainless steel reactor; Γ_{out}: boundary between Ω_2 and hot oil (convective heat flux); Γ_{in}: boundary between Ω_1 and Ω_2 (thermal contact resistance) and Γ_{sym} symmetry surface (no flux).

RESULTS & DISCUSSION

Monomeric anthocyanin content ($A^{(t)}$) was measured experimentally in the blackberry juice – quartz sand samples at low water activity for different time-temperature treatments at 100, 120 and 140 °C. A non-isothermal method was used to estimate kinetic parameters (k_{ref} and E_a) considering a homogeneous and a heterogeneous temperature distribution inside the reactor. The results showed no significant difference between the anthocyanins degradation reaction rate constant ($k_{120°C}$) for the heterogeneous (k_{ref}=3.29±0.05×10^{-3} s^{-1}) and the homogeneous (k_{ref} =3.5±0.3×10^{-3} s^{-1}) assumption. And a slight difference was found between the activation energies (E_a) for the heterogeneous (E_a=95±5 kJ mol^{-1}) and the homogeneous (E_a=108±7 kJ mol^{-1}) identification. Therefore, the use of the developed model allowed a slight improvement in the identification of the kinetic parameters.

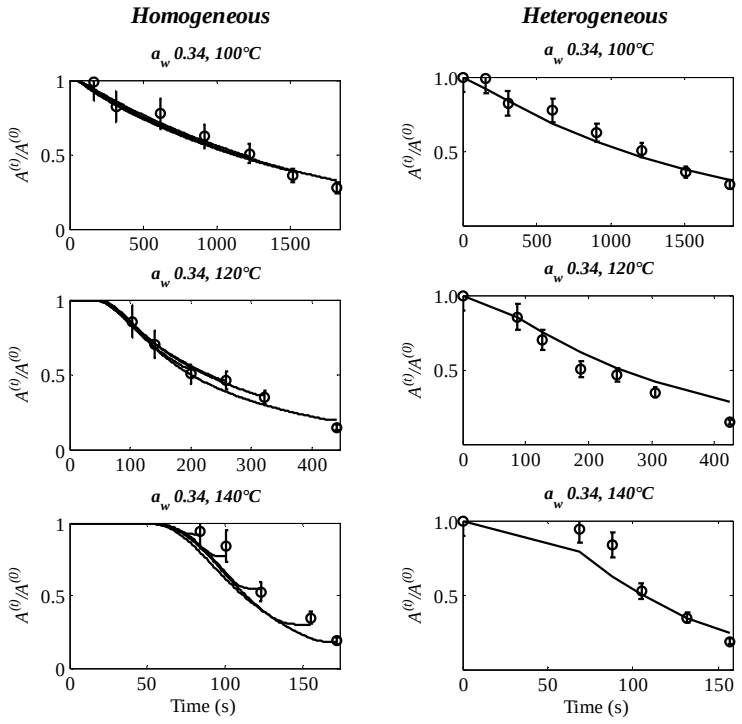

Figure 2. Degradation kinetics of monomeric anthocyanins ($A^{(t)}/A^{(0)}$) from blackberry juice – quartz sand samples at initial a_w 0.34 during heat treatments from 100 to 140 ºC in a hermetically sealed reactor. Experimental data (O) and predicted curves for each trial for the homogeneous and heterogeneous temperature distribution assumption. Bars represent 95% confidence interval (n = 5).

Figure 2 shows that the reaction kinetics during 100–140 °C heat treatments were well represented by first-order reactions, as a good fit is observed between experimental data and the lower end of predicted curves. Moreover, low root mean square errors ($RMSE \leq 0.08$) were obtained, which means that the absolute mean error between experimental and predicted values was less than 8%.
The improvement in the identification of the kinetic parameters was not substantial in the case of the anthocyanins degradation at high temperatures, considering the complexity of the heterogeneous approach compared to the homogeneous assumption. Therefore, it is interesting to identify under what conditions the heterogeneous approach is worthwhile.

Figure 3 shows a series of combinations of kinetic parameters (k_{ref} and E_a) to assess the impact of using the heterogeneous method instead of the homogeneous approach in the kinetic parameter identification of a compound *X*. **Figure 3*a*** and **3*b*** present the Arrhenius plot describing the temperature dependence of k_X at four activation energies (E_a=50 to 300 kJ mol^{-1}) with the same k_{ref}=3×10^{-3} s^{-1} (**3*a***), and at four rate constants (k_{ref} =1×10^{-4} to 1×10^{-1} s^{-1}) with an equal E_a=100 kJ mol^{-1} (**3*b***), giving a total of eight combinations of kinetic parameters. **Figure 3*c*** and **3*d*** represent the simulated temperature profile ($T^{(t)}$) applied to compound *X* at the "cold point" of the reactor for a product at initial a_w 0.34 heated at 140 °C, considering the same thermophysical properties and thermal parameters of the previous analysis.

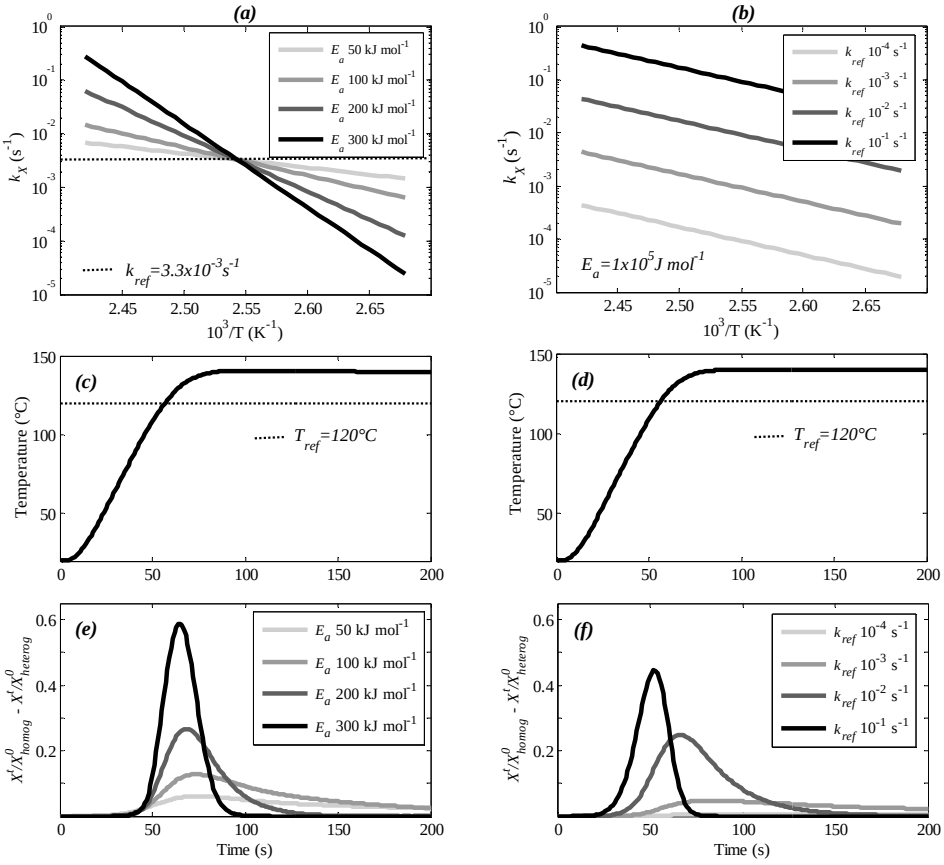

Figure 3. Arrhenius plot describing the temperature dependence of k_X at four activation energies (E_a=50–300 kJ mol^{-1}) with the same k_{ref}=3×10^{-3} s^{-1}(*a*), and at four rate constants (k_{ref}=10^{-4}–10^{-1} s^{-1}) with E_a=100 kJ mol^{-1} (*b*). Simulated temperature profile ($T^{(t)}$) applied to compound *X* at the "cold point" of the reactor heated at 140 °C (*c* and *d*), and gap between the degradation kinetics of the compound *X* ($X^{(t)}/X^{(0)}$) estimated under homogeneous and heterogeneous temperature distribution within the sealed reactor for the previous kinetic parameters (*e* and *f*).

Finally, **Figure 3*e*** and **3*f*** show the gap between the degradation kinetics of the compound X ($X^{(t)}/X^{(0)}$) estimated under homogeneous and heterogeneous temperature distribution within the sealed reactor for each combination of kinetic parameters. From the simulations is observed that, the higher the kinetic parameter (E_a and k_{ref}), the greater the error made when using the homogeneous approach. The difference between the concentration of X simulated under homogeneous and heterogeneous temperature distribution assumption, could reach nearly 60% for the higher activation energy combination (E_a=300 kJ mol^{-1} and $k_{120°C}$=3×10^{-3} s^{-1}) and 45% for the higher reaction rate constant at T_{ref}=120 °C (k_{ref}=1×10^{-1} s^{-1} and E_a=100 kJ mol^{-1}), under these conditions it would indeed be justified using the heterogeneous approach. These orders of magnitudes of kinetic parameters are characteristic of microbial inactivation and protein denaturation [1].

CONCLUSION

Kinetic modelling was conducted to develop a useful tool, which, in association with a heat transfer model, could predict compounds degradation under non-isothermal conditions in intermediate moisture food, commonly used in agro-industry. The application of the kinetic model allows the generation and adjustment of temperature profiles of heat processes to better achieve expected results. Such results may include the improved preservation of the nutritional qualities of heat-sensitive fruits and vegetables during high-temperature processing.

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